Research and Development of High Temperature Resistant Polymeric Film Forming Materials

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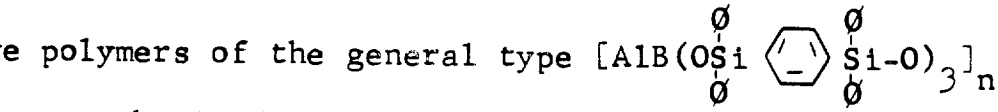
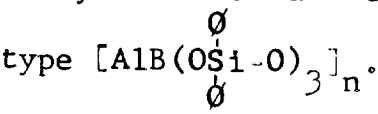
Preface

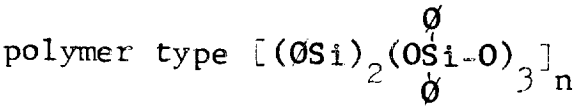
This monthly progress report was prepared by the Stauffer Chemical Company at Weston, Michigan. The work was done for the George C. Marshall Space Flight Center in connection with Contract NAS8-1532. The work is directed toward preparation of heat resistant polymeric film forming materials and it is under the technical cognizance of Mr. James Curry of the Propulsion and Vehicle Engineering Division of the Space Flight Center.

Contents

Abstract

Five polymers of the general type  have been synthesized and compared to previously reported polymers of the type  .

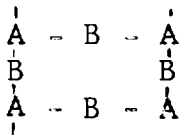
In general they were found to be similar in respect to thermal stability, physical form and film forming properties.

The polymer type  which is also a combination of di and tri functional groups is reported as having desirable characteristics.

Discussion

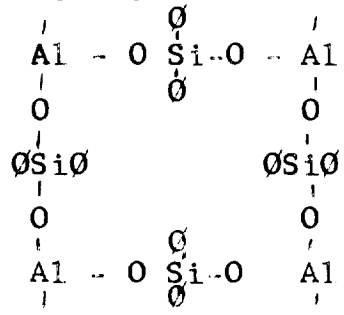
The goal of the over all research project under Contract NAS8-1532 is to produce polymeric materials which can be adapted for use as a resinous pigment holder. This resinous vehicle should preferably be non absorbing or non reflecting of the radiation present above the atmosphere. For this reason the chelated metal might contain a built-in handicap since it appears to be always colored ie. selective absorption in the visible wave lengths. The chelated metal type polymer exhibits commendable heat and thermal stability but because of the color, efforts have been directed towards finding a polymer which has equal stability and is at the same time colorless to the visible spectrum.

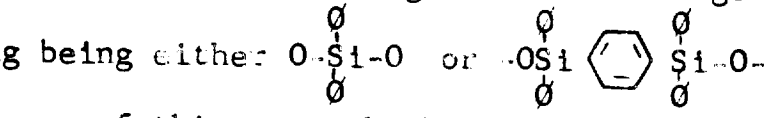
The work has now progressed to where it is appropriate to report this work more fully. The polymers built from a combination of di and trifunctional groups are believed to be of the general structure illustrated



thus producing a crosslinking of two linear polymers. Until the structure is more accurately known it shall be thought of as a ladder.

Tri functional boron, aluminum or combinations of both were used with difunctional silicon phenyl groups to afford polymers which are probably structured as shown



with aluminum and boron being used interchangebly and the silicon grouping being either  or

Polymers of this type which are reported at this time were found to be fairly stable in the 400-500°C range and to be sufficiently soluble, in most cases, to form films by solvent evaporation. Also it was observed that the film was clear and nearly colorless.

A variation of this where the tri functional group was silicon ie. ØSi≡ was also tried with promising results although the work is not far enough along to warrent full confidence in an optimum outcome. At this time it appears that such compounds might have very good heat stability but they may have low softing temperatures, perhaps as low as body temperature for some.

The work done in the period covered by this report is described by the experimental proceedures and the table of physical characteristics which follow. It will be seen that boron analyses are missing. This subject was discussed at some length in the previous report where it was explained that a gravimetric analysis involving a boron atom is not feasible and it must be done separately by titration. This phase has not been completed.

Experimental

$[Al_2B_4(OSi(\phi_2)-O)_9]_n$ Ref: 3-114-72, 4-128-24.

The repetition synthesis was completed to correct stoichiometry. Freshly distilled aluminum isopropoxide 5.37 grams (.0263 mole) was dissolved in 60 ml of dry n-heptane. Boron triisopropoxide 9.89 grams (.0526 mole) and diphenyl silane diol 25.61 grams (.1184 mole) were combined with 75 ml benzene, the aluminum isopropoxide and all were placed in a 250 ml, 3 neck flask. The materials were refluxed four hours and then stripped of solvents up to 200°C/1 mm Hg. 80.7% yield of solids was achieved. The polymer has identical characteristics to those described in the March Report page 9-10. Ref: 3-114-72. Ratio of Al to Si found, 1:4.7; calculated, 1:4.6.

$B(OSi\phi_3)_3$ Ref: 1-128-27

This model compound was synthesized for infra-red studies only. Triphenyl chloro silane 10 grams in a 250 ml flask equipped with a funnel, reflux condenser and agitation. To this was added ammonium hydroxide solution 1:1 (35 ml) at a rapid rate until the solution was alkaline(pH 8). It was refluxed 15 minutes, cooled, the water-organic phases separated and the ether evaporated. The solids were redissolved in a minimum amount (1 gram/4ml) hot benzene, a few ml of pet ether was added and it was set aside to crystallize. The triphenyl silanol so produced was dried of benzene solvent and used as follows.

$$B(OC\text{-}(CH_3)_2)_3 + 3\emptyset_3SiOH \longrightarrow B(OSi\emptyset)_3 + 3(CH_3)_2CHOH\uparrow$$

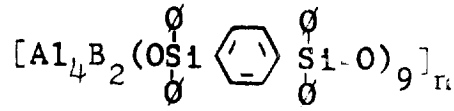
Boron isopropoxide 1.27 grams in 25 ml n-heptane was combined with triphenyl silanol 5.58 grams in 50 ml of benzene while the boron isoproxide was refluxing. The isopropanol was distilled off as it was produced. Twenty five ml additional benzene was required to complete the removal of isopropanol. The solvent remaining was removed leaving a white solid with melting point of 125-150°C. The crude yield was 97%. A small sample was recrystallized from benzene and submitted for I-R analysis. Analysis for silicon found 11.13%, calculated for product 10.07%.

$[Al_4B_2(O\overset{\emptyset}{\underset{\emptyset}{Si}}O)_9]_n$ Ref: 1-114-68 and 2-114-80 (Repeat).

Aluminum isopropoxide 5.08 grams (.0249 mole) in 100 ml n-heptane was combined with boron isopropoxide 2.35 grams (.0125 mole) in 60 ml bnezene and 12.12 grasm (.0560 mole) of diphenyl silandiol. The materials were refluxed 5 hours, the solvent removed and dried up to 200°C/1 mm Hg. Yield 73.1%. Some observed physicals are recorded in Table I. Ratio of Al to Si found 1:2.30, calculated ratio 1:2.34.

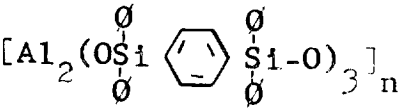
$[Al_2(O\overset{\emptyset}{\underset{\emptyset}{Si}}\text{-}O)_3]_n$ Ref: 1-114-63, 2-114-66 and 4-114-81 (repeat).

Aluminum isopropoxide 6.44 grams (.0473 mole) of diphenyl silane diol were mixed and refluxed for 8 hours. The solvents were then removed and the residue dried at 200°C/1 mm Hg to produce 8.57 grams (73% theory) yield. Table I lists the observed physical characteristics. Ratio of Al to Si found 1:1.49, calculated ratio 1:1.56.



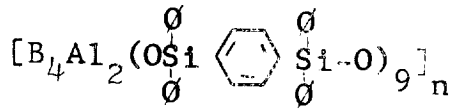
Ref: 1-128-30

Aluminum isopropoxide (freshly distilled) 4.18 grams (.0205 mole) in 100 ml of n-heptane was placed in a 250 ml 3 neck flask equipped with agitator, reflux condenser and nitrogen inlet. Boron isopropoxide 1.92 grams (.0102 mole) in 60 ml of benzene was added. To this stirred solution 21.79 grams (.0459 mole) of bis 1-4(diphenyl-hydroxy silyl) benzene was added incrementally as a dry powder while the solution was refluxing. The solvents were then removed by distillation and the residue dried to 60°/1 mm Hg. for 1 hour for a 79% crude yield. See Table I for physical characteristics. Ratio of Al to Si found 1:4.0, calculated 1:~~4.7~~ 4.5.



Ref:1-128-26

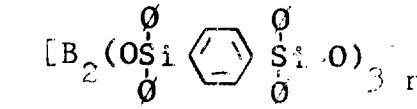
Aluminum isopropoxide 6.72 grams (.033 mole) was distilled into a 250 ml 3 neck flask and dissolved in 125 ml of n-heptane. Bis-1-4(diphenyl hydroxy silyl) benzene 23.4 grams (.0493 mole) was added incrementally and then the whole was refluxed @ 93.97°C for four hours. The solvents were stripped off and the residue dried to 210°C/.5 mm Hg. Crude yield 16.8 grams (70% theory). See Table I for physical data. Ratio of Al to Si found 1:3.12, calculated ratio 1:3.



Ref 1-128-29

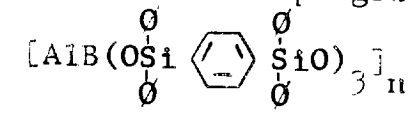
Aluminum isopropoxide 2.19 grams (.0107 mole) was distilled into a nitrogen purged 3 neck 250 ml flask. Benzene, 60 ml, and boron isopropoxide 403 grams (.0214 mole) in 100 ml of benzene was added.

To this refluxing mixture 22.88 grams (.0482 mole) of bis 1-4(diphenyl hydroxy silyl) benzene was added incrementally and then refluxed four hours longer. The solvents were removed, the residue dried @ 200°C/1mm Hg to produce 14.24 grams (60% theory) crude yield. See Table I for description of physical data. Ratio of Al to Si found 1:9.4, calculated ratio 1:9.3.



Ref: 1-114-85

Boron isopropoxide 5.73 grams (.0305 mole) in 140 ml of dried benzene and 21.56 grams (.0456 mole) of bis 1-4(diphenyl hydroxy silyl) benzene were added to a 250 ml 3 neck flask equipped with a partial take off distilling head. The isopropanol-benzene azeotrope was removed in an eight hour reflux period. The remaining solvents were removed and the residue dried @ 250°C/ 1 mm Hg, to produce 19.6 grams (90% theory) yield of glass like polymer. Some physical characteristics are noted in Table I. Analysis for boron is in progress.



Ref: 1-114-86

Freshly distilled aluminum isopropoxide 3.69 grams (.0181 mole) in 75 ml n-heptane, 2.70 grams (.0181 mole)of boron isopropoxide in 75 ml benzene and 25.78 grams (.0543 mole) of bis 1-4(diphenyl-hydroxy silyl) benzene were refluxed together for 5 1/2 hours. The azeotropic isopropanolwas removed followed by removal of the remaining benzene. The residue was dried @ 250°C/1 mm Hg to produce 20.70 grams (79% theory) of amber colored solids. See table I.

Ratio of Al to Si found 1:6.20, calculated ratio 1:6.25.

$[(\text{ØSi})_2(\text{O}\overset{\text{Ø}}{\underset{\text{Ø}}{\text{Si}}}\text{-O})_3]_n$ Ref: 1-128-25

Phenyl triethoxy silane 12 grams (.0499 mole) in 100 ml dry benzene was placed in a 250 ml flask equipped with condenser and agitator. To this was added 16.2 grams (.0748 mole) of diphenyl silane diol incrementally as a dry powder. The diol was rinsed in with 100 ml n-heptane and all was refluxed for 3 hours. The solvents were stripped down to 50 ml and 150 ml of xylene added. Continued refluxing @ 97°C for five hours appeared not to promote any further reaction but removal of residual heptane caused the temperature to rise to 135°C whereupon the solution cleared and the xylene was removed after an additional 3 hour reflux. The remaining solids weighed 9.1 grams (42.7% theory). Silicon analysis 15.81% Calculated Si 16.46%. See Table I.

$[(\text{MeSi})_2(\text{O}\overset{\text{Ø}}{\underset{\text{Ø}}{\text{Si}}}\text{-O})_3]_n$ Ref: 1-114-87

Methyl triethoxy silane 6.00 grams (.0681 mole) in 150 ml dry benzene and diphenyl silane diol 11.10 grams (1.021 mole) were added to a flask equipped with a partial take off distilling head. It was refluxed for one hour, stripped of all solvents and dried to 200°C/1 mm Hg. The glass-like residue (18.37 grams) represented a 74% yield. See Table I. Silicon analysis is in progress.

The Intermediate $\text{HO}\overset{\text{Ø}}{\underset{\text{Ø}}{\text{Si}}}\langle\_\rangle\overset{\text{Ø}}{\underset{\text{Ø}}{\text{Si}}}\text{-OH}$ Ref: 5-114-82

N-Butyl ether (1 mole) produced from 15.2 grams of cut lithium wire and 1 mole butyl bromide in 500 ml ether @ -7°C was reacted with 1-4 dilithiobenzene. This was transferred under argon to a

separatory funnel (chilled to 0°C) from where it was added to a solution of diphenyl dichlorosilane in 500 ml ether @ 0°C. The bis 1-4(diphenylchlorosilyl) benzene so produced was hydrolyzed in situ by the slow addition of 1 liter of 5% HCl solution in water. It was allowed to warm to room temperature after an hour of stirring. The two layers were separated and the ether phase washed with Na_2CO_3 solution until it was near neutral to pH paper. The ether phase was reduced in volume to 1/2 and ca. 1 liter of pet ether was added to produce 70 grams. The washings were processed to produced an additional 25 grams for a 40% yield. M.p. 149-160°C. Si 11.80%. Calculated for product 11.84%.

Ref:	Formula	Characteristics				Solubility in grams/100 ml *less than 5 g/100 ml						
		Color	Form	Film	Heat Test	Acetone	Ether	Ethanol	Benzene	Heptane	THF	DMF
3-114-72 4-128-24	$\left[Al_2B_4(O\text{-}Si\text{-}O)_9\right]_n$ (Ø)	cream white	glass	solvent	500°C/1mm Hg 22% wt loss	8	*	*	*	*	8	10
1-128-27	$B(OSi\phi_3)_3$	clear	glass	- -	- - -	-	-	-	-	-	-	-
2-114-80 1-114-68	$\left[Al_4B_2(OSi\text{-}O)_9\right]_n$ (Ø)	white	glass	solvent	500°C/1mm Hg 15.8% wt loss	5	*	*	*	*	5	6
1-114-63 2-114-66 4-114-81	$\left[Al_2(O\text{-}Si\text{-}O)_3\right]_n$ (Ø)	cream white	glass	no	550°C/1 mm Hg 15.5% wt loss	*	*	*	*	*	*	*
1-128-30	$\left[Al_4B_2(O\text{-}Si\text{-}C_6H_4\text{-}Si\text{-}O)_9\right]_n$ (Ø)	white	powder	solvent	500°C/1 mm Hg 17.9% wt loss	*	*	*	*	*	8	10
1-128-26	$\left[Al_2(OSi\text{-}C_6H_4\text{-}Si\text{-}O)_3\right]_n$ (Ø)	pale yellow	powder	no	460°C/1mm Hg 14.3% loss	*	*	*	*	*	*	*
1-128-29	$\left[Al_2B_4(OSi\text{-}C_6H_4\text{-}Si\text{-}O)_9\right]_n$ (Ø)	white	glass	solvent	510°C/1mm Hg 24.8% wt loss	10	*	*	6	*	10	10
1-114-85	$\left[B_2(OSi\text{-}C_6H_4\text{-}Si\text{-}O)_3\right]_n$ (Ø)	white	glass	solvent & melt	400°C/1 mm Hg 3.24% wt loss melts 170°C	10	10	*	10	*	10	10
1-114-86	$\left[AlB(OSi\text{-}C_6H_4\text{-}Si\text{-}O)_3\right]_n$ (Ø)	white	glass	solvent	460°C/1 mm Hg 16.5% wt loss	10	*	*	10	*	10	10
1-128-25	$\left[(\phi Si)_2(OSi\text{-}O)_3\right]_n$ (Ø)	amber	glass	solvent & melt	460°C/1 mm Hg 12.6% wt loss m.p. 80°C	10	10	*	10	*	10	10
1-114-87	$\left[(MeSi)_2(-O\text{-}Si\text{-}O)_3\right]_n$ (Ø)	amber	glass	melt & solvent	520°C/1 mm Hg 11.35% wt loss m.p. 200°C	20	10	*	14	*	16	16
5-114-82	$HOSi\text{-}C_6H_4\text{-}Si\text{-}OH$ (Ø)	white	cryst.	--	m.p. 150-165°C	-	-	-	-	-	-	-

Plans for Work During the Period May 1 to May 18, 1963

The emphasis, of course, will be directed towards the completion of loose ends which may have accumulated throughout the contract year. This is a necessary effort in order to make the final report as complete and useful as possible. Some of the more evident uncompleted phases are -

a) incomplete film forming property evaluation of $[(C_9H_6NO)_2Si\text{-}O]_n$ Ref: 1-114-64.

b) incomplete evaluation of film forming properties and heat stabilities of $[(MeSi)_2(O\overset{\emptyset}{\underset{\emptyset}{Si}}\text{-}O)_3]_n$ Ref: 1-114-87

c) synthesis of the polymer $[(\emptyset Si)_2(O\text{-}\overset{\emptyset}{\underset{\emptyset}{Si}}\text{-}C_6H_4\text{-}\overset{\emptyset}{\underset{\emptyset}{Si}}\text{-}O)_3]_n$

in order to evaluate it against $[(\emptyset Si)_2Si(O\overset{\emptyset}{\underset{\emptyset}{Si}}\text{-}O)_3]_n$ Ref: 1-128-25

d) photograph and print I-R scans of representative polymers and monomers for inclusion in the final report. The work is now complete except for the part of the photographer.

e) start writing the final report with a target date of completion, for the editing copy, May 28, 1963.